

**Pharmaceuticals and Personal Care Products in Archived U.S. Biosolids from the
2001 EPA National Sewage Sludge Survey**

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10 Pages

Supplementary Information

Sample analysis. Composite sludges were divided into two aliquots of up to 1 g dry solids, and adjusted for pH with phosphate buffer and ammonium hydroxide, respectively, prior to acid and base extraction. Acidic and base fractions were spiked with stable isotope-labeled surrogate standards of the target analytes. Both fractions were sonicated and extracted three times with a phosphate buffer/acetonitrile solution for the acid fraction, and with an ammonium hydroxide/acetonitrile solution for the base fraction. Then, both fractions were concentrated to remove acetonitrile and re-diluted with reagent water. For acid extraction Na₄EDTA was added for stabilization. Both the acid fraction and the base fraction were cleaned using a solid-phase extraction (SPE) hydrophilic-lipophilic balance (HLB) 20ccm cartridges containing 1 g of resin. The acid fraction was washed with reagent water to remove EDTA, and the analytes were eluted with methanol. In addition, triclocarban and triclosan were eluted with a mixture of equal parts of acetone and methanol. The base fraction was eluted with methanol followed by 2% formic acid. After extraction, both fractions were concentrated under a nitrogen atmosphere and reconstituted in methanol. Internal standards were added to both fractions just prior to analysis.

For the purpose of compound detection, the 72 analytes were divided into four groups. All analytes were separated by liquid chromatography and detected by tandem mass spectrometry. Groups 1 – 3 were extracted under acidic conditions at pH 2. Groups 1 and 2 were analyzed in positive electrospray ionization (ESI) mode, with Group 2 being specific to tetracyclines. Group 3 was analyzed in negative ESI mode. Group 4 was extracted under basic conditions at pH 10 and analyzed in positive ESI mode.

Table S1. Facilities Sampled in the 2001 National Sewage Sludge Survey

facility name	city	state	facility name	city	state
Sacramento Regional WWTP	Elk Grove	CA	Metropolitan Council – Metro	Saint Paul	MN
Fallbrook Public Utility District	Fallbrook	CA	Crocker WWTP	Crocker	MO
Manteca WQCF	Manteca	CA	Mason Farm WTP	Carrboro	NC
Central Contra Costa Sanitary District	Martinez	CA	Whiteville WWTP	Whiteville	NC
Fairfield Suisun Sewer District	Suisun city	CA	Burwell WWTF	Burwell	NE
Boulder – 75 th St WWTP	Boulder	CO	Middletown Sewerage Authority	Belford	NJ
Steamboat Springs	Steamboat Springs	CO	Joint Meeting Treatment	Elizabeth	NJ
Rocky Hill WPCP	Hartford	CT	Passaic Valley Sewerage Commision	Newark	NJ
Waterbury WPCF	Waterbury	CT	Bowery Bay WPC	Corona Queens	NY
DC WASA (Blue Plains)	Washington	DC	Hunt's Point WPC	Corona Queens	NY
Mulberry STP	Mulberry	FL	Cayuga Heights WWTP	Ithaca	NY
Escambia County – Main Street WTP	Pensacola	FL	Brewster WWTP	Mahopac	NY
St. Petersburg SW Treatment Plant	St. Petersburg	FL	NEORSD – Southerly	Cleveland	OH
Sunrise Sweage Treatment Plant No. 1	Sunrise	FL	Brentwood Estates STP #24	Cuyahoga Falls	OH
R.M. Clayton WPCP	Atlanta	GA	Delphos	Delphos	OH
Buford Westside WPCP	Buford	GA	Massillon	Massillon	OH
Cartersville WPCP	Cartersville	GA	North Olmsted	North Olmsted	OH
Dekalb Co – Snapfinger Cr WPCP	Decatur	GA	Port Clinton	Port Clinton	OH
Garden City WPCP	Garden City	GA	Twin Lakes WWTP	Ravenna	OH
Gwinnett Co Jackson Cr	Lilburn	GA	Thornville	Thornville	OH
Ocmulgee WPCP	Warner Robins	GA	West Carrollton	West Carrollton	OH
Boise	Boise	ID	Blackwell	Blackwell	OK
Belleville STP #1	Belleville	IL	Lebanon	Lebanon	OR
MWRDGC Stickney STP	Cicero	IL	Portland	Portland	OR

Jacksonville STP	Jacksonville	IL	Burnham STP	Burnham	PA
Morris STP	Morris	IL	Downington Area Regional Authority	Downington	PA
Tolono STP	Westville	IL	Girard Boro	Girard	PA
Evansville STP – Westside	Evansville	IN	Kiski Valley Water Pollution Control	Leechburg	PA
Frankton Municipal STP	Frankton	IN	Philadelphia Water Dept (SW)	Philadelphia	PA
Hammond Municipal STP	Hammond	IN	Philadelphia Water Dept (NE)	Philadelphia	PA
Muncie Sanitary District	Muncie	IN	Allengheny County Sanitary Authority	Pittsburgh	PA
Terre Haute Municipal STP	Terre Haute	IN	Narragansett Bay Commission – Bucklin	Providence	RI
Union city Municipal STP	Union City	IN	Florence – Pee Dee River Plant	Florence	SC
Oakland STP	Topeka	KS	WCRSA/Pelham WWTF	Greenville	SC
Shepherdsville STP	Shepherdsville	KY	Brooking	Brookings	SD
Billerica WWTP	Billerica	MA	Sioux Falls	Sioux Falls	SD
Fall River WWTF	Fall River	MA	Andrews STP	Andrews	TX
Medfield WWTP	Medfield	MA	Del Rio – San Felipe	Del Rio	TX
Pittsfield WWTP	Pittsfield	MA	Navasota, Grimes Co. STP	Navasota	TX
Patapsco WWTP	Baltimore	MD	Orange, Jackson St WWTP	Orange	TX
South Portland WPCF	South Portland	ME	Brazos River Authority (Waco)	Waco	TX
Dowagiac WWTP	Dowagiac	MI	Fredericksburg City STP	Fredericksburg	VA
Iron Mountain – Kingsford WWTP	Kingsford	MI	Augusta County Service Authority	Verona	VA
Genesee County – Ragnone WWTP	Montrose	MI	HRSD – James River STP	Virginia Beach	VA
Port Huron WWTP	Port Huron	MI	HRSD – Chesapeake/Elizabeth STP	Virginia Beach	VA
Wyandotte WWTP	Wyandotte	MI	Metropolitan King County	Renton	WA
Western Lake SSD	Duluth	MN	Greenbrier County PSD No 2	Rainelle	WV

Table S2. Summary of Analytical Results of Pharmaceuticals and Personal Care Products that Were Not Detected in Sewage Sludge, along with their Use and Effect Concentrations for Aquatic Organisms where available.

substance name	CAS RN	detection limit [$\mu\text{g kg}^{-1}$]	standard deviation detection limit	recovery [%]	isotope dilution quantification	use	Effect concentration aquatic biota [$\mu\text{g L}^{-1}$]
acetaminophen	103-90-2	225	64.0	97	✓	antipyretic	13 000 ^a (Kuhn et al., 1989)
albuterol	18559-94-9	3.4	0.7	96	✓	antiasthmatic	
anhydro-chlortetracycline	4497-08-9	64.0	8.5	75		antibiotic	
carbadox	6804-07-5	22.6	10.8	106		antibiotic	
cefotaxime	63527-52-6	90	33.1	181		antibiotic	
clinafloxacin**	105956-97-6	35.5	13.9	297		antibiotic	50 000 ^a (Williams et al., 1992)
cloxacillin	61-72-3	25.9	5.8	87		antibiotic	
dehydronifedipine	67035-22-7	2.5	0.3	131		nifedipine metabolite	
demeclacycline	127-33-3	61.3	7.8	68		antibiotic	
digoxigenin	1672-46-4	62.1	10.8	111		digoxin metabolite	
digoxin	20830-75-5	108	25.1	61		antiarrhythmic	24 209 ^a (Lilius et al., 1994)
1,7-dimethylxanthine	611-59-6	581	161	97		caffeine metabolite	
4-epianhydro-chlortetracycline*	158018-53-2	250	56.0	20		antibiotic	
4-epoxytetracycline	14206-58-7	28.0	6.4	90		antibiotic	
flumequine	42835-25-6	6.7	0.8	106		antibiotic	159 ^b (Luetzhoff et al., 1999)
lincomycin	154-21-2	13.1	1.5	78		antibiotic	
norgestimate	35189-28-7	22.6	4.9	103		contraceptive	
ormetoprim	6981-18-6	2.2	0.6	101		antibiotic	
oxacillin	66-79-5	11.6	2.5	111		antibiotic	
oxolinic acid	14698-29-4	2.9	0.5	96		antibiotic	180 ^b (Luetzhoff et al., 1999)
penicillin G	61-33-6	11.2	3.2	108		antibiotic	

penicillin V	87-08-1	22.5	6.4	126		antibiotic	
roxithromycin	80214-83-1	3.0	0.7	100		antibiotic	
sarafloxacin**	98105-99-8	173	50.4	214		antibiotic	
sulfachloropyridazine	80-32-0	5.6	1.6	109		antibiotic	
sulfadiazine	68-35-9	5.6	1.6	105		antibiotic	135 ^b (Luetzhoft et al., 1999)
sulfadimethoxine	122-11-2	2.1	0.4	94		antibiotic	50 000 ^c (Forni et al., 2002)
sulfamerazine	127-79-7	2.3	0.5	94		antibiotic	> 100 000 ^d (Bills et al., 1993)
sulfamethazine	57-68-1	4.0	0.9	102	✓	antibiotic	> 100 000 ^e (Davis and Hidu, 1969)
sulfamethizole	144-82-1	3.4	0.9	75		antibiotic	
sulfathiazole	72-14-0	5.8	1.5	84		antibiotic	
tylosin	1401-69-0	397	136	102		antibiotic	54 700 ^f (Halling-Sorensen et al., 1998)
virginiamycin	11006-76-1	82.7	31.2	110		antibiotic	
warfarin	81-81-2	5.3	1.6	119	✓	anticoagulant	88 799 ^a (Lilius et al., 1994)

a, crustacean; *b*, cyanobacteria; *c*, aquatic plant; *d*, fish; *e*, mollusk; *f*, sludge bacteria

* concentration may be underestimated due to low recovery rate in quality control sample

** concentration may be overestimated due to high recovery rate in quality control sample

Table S3. Quality Control Acceptance Criteria for Ongoing Precision and Recovery Analysis.

Substance name	Recovery control limits (%)	Substance name	Recovery control limits (%)	Substance name	Recovery control limits (%)
acetaminophen	50-120	doxycycline	22-166	oxolinic acid	42-124
albuterol	50-133	enrofloxacin *	50-125	oxytetracyclin	50-183
anhydrochlortetracycline	50-135	4-epianhydrochlortetracycline	18-120	penicillin G	5-200
anhydrotetracycline	7-141	4-epianhydrochlortetracycline	5-200	penicillin V	5-200
azithromycin	33-120	4-epichlortetracycline *	50-150	ranitidine	24-160
caffeine	50-124	4-epoxytetracycline	50-142	roxithromycin	38-120
carbadox	33-144	4-epitetraacycline	50-173	sarafloxacin	17-200
carbamazepine	21-137	erythromycin-H2O	50-158	sulfachloropyridazine	50-200
cefotaxime	8-186	flumequine	36-200	sulfadiazine	5-200
chlortetracycline *	45-172	fluoxetine	49-125	sulfadimethoxine	50-120
cimetidine	5-120	gemfibrozil	50-120	sulfamerazine	50-148
ciprofloxacin	50-120	ibuprofen *	50-120	sulfamethazine	50-142
clarithromycin	8-154	isochlortetracycline *	5-200	sulfamethizole	50-120
clinafloxacin	5-200	lincomycin	5-120	sulfamethoxazole *	50-120
cloxacillin	5-200	lomefloxacin *	17-200	sulfanilamide *	5-189
codeine *	34-129	metformin *	50-149	sulfathiazole	41-120
cotinine	50-124	miconazole	27-120	tetracycline	50-155
dehydronifedipine	42-120	minocycline *	5-176	thiabendazole	50-120
demeclocycline	5-200	naproxen	5-120	triclocarban	50-120
digoxigenin	8-183	norfloxacin	50-135	triclosan	50-120
digoxin	5-148	norgestimate	36-120	trimethoprim *	50-126
diltiazem	11-120	ofloxacin	50-200	tylosin	16-149
1,7-dimethylxanthine	50-138	ormetoprim	5-120	virginiamycin	5-189
diphenhydramine	48-120	oxacillin	50-200	warfarin	50-120

Table S4. Overview of the Ten Most Abundant PPCPs Found in the Present Study and their Previously Reported Concentrations in Sewage Sludge.

substance name	mean concentration in present study [$\mu\text{g kg}^{-1}$ dry weight]	reported concentration in sewage sludge [$\mu\text{g kg}^{-1}$ dry weight]	reference
triclocarban	36,000	51,000 19,300 2,170 – 5,970	(Heidler et al., 2006) (Sapkota et al., 2007) (Chu and Metcalfe, 2007)
triclosan	12,600	530 - 15,600	(McAvoy et al., 2002)
		29,000	(USEPA, 2003)
		620 – 11,550	(Chu and Metcalfe, 2007)
		30,000 10,500	(Heidler and Halden, 2007) (Kinney et al., 2008)
ciprofloxacin	6,900	60 – 2420 500 – 4800 9,300 – 11,700 1,400 – 2000	(Golet et al., 2002) (Lindberg et al., 2005) (Lindberg et al., 2006) (Lindberg et al., 2007)
ofloxacin	5,400	n.d. – 2000	(Lindberg et al., 2005)
4-epitetracycline	2,300	Not reported	
tetracycline	1,900	Not reported	
minocycline	1,900	Not reported	
diphenhydramine	1,200	7000	(Kinney et al., 2008)
doxycycline	1,000	n.d. – 1500	(Lindberg et al., 2005)
azithromycin	800	64 n.d. – 158 14 – 25	(Gobel et al., 2005) (Gobel et al., 2005) (Jones-Lepp and Stevens, 2007)

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